

By: F. H. Schubert and R. A. Wynveen

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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DEVELOPMENT OF A  
LABORATORY BREADBOARD MODEL OF A  
CHLORINE GENERATING DEVICE TO CHLORINATE  
RECLAIMED WATER ON A SPACECRAFT

FINAL REPORT

By: F. H. Schubert and R. A. Wynveen

December, 1970

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Cleveland, Ohio 44122

for

LANGLEY RESEARCH CENTER  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## SUMMARY

A need exists to retain a water's potability once it has been reclaimed aboard a space vehicle. Past efforts have used thermal storage or a silver ion generator to accomplish this. The thermal storage method has a considerable power penalty. The silver ion generator method has shown limited applicability.

Water chlorination is the most widely used method. Its application to the water reclamation process of advanced life support systems has not been attempted because of past difficulties in developing a reliable and simple electrolytic chlorine ( $\text{Cl}_2$ ) generator. Also, there have been difficulties in developing a low rate feed device. The current program represents a first step in the development of such a  $\text{Cl}_2$  supply. It would allow in-flight generation of  $\text{Cl}_2$  at the time and only in the amount needed.

The device consists of three series electrolytic cells. A  $\text{Cl}_2$  generator that produces a  $\text{Cl}_2$  flowrate proportional to current and quantity proportional to the integration of current over time. A by-product, hydrogen ( $\text{H}_2$ ) gas, is also produced. This  $\text{H}_2$  is immediately consumed in the second electrolytic cell. The third cell is an electrochemical valve that also performs a  $\text{Cl}_2$  flow metering function.

During the program a laboratory breadboard of the system was designed and tested. It consisted of the three cells integrated together and a test control and instrumentation console. The latter was used to obtain characterization data during the test program.

The total power required by the three components was less than  $\frac{1}{2}$  watt--0.2 watts for the generator, 0.02 watts for the valve and no power required by the eliminator. The gases were found to be generated in a pure form. No  $\text{Cl}_2$  or other gas was evolved with the  $\text{H}_2$ . No oxygen ( $\text{O}_2$ ) or other gas was evolved with the  $\text{Cl}_2$ .

A continuous operating test was carried out after the parametric studies. A total of 788 hours were accumulated prior to shutdown for materials evaluation. The selected materials of construction were found to be stable. Use of platinum black was observed not to be necessary for performance. The device is ready for integrating into a complete water disinfecting system. A minimum form of the latter includes a  $\text{Cl}_2$ -into-water dispenser and a chlorination level detector and feedback control loop in addition to the electrolytic feed supply.

## 1.0 INTRODUCTION

### 1.1 Background

An adequate supply of potable water is an essential requirement for a spacecraft. The occupants must have water for drinking, food preparation, washing and other sanitary purposes. Thus, potable water recovery is an essential part of an advanced life support system. Maintaining the recovered water potable is equally important.

Two methods for maintaining water potability have received the most attention--thermal storage and use of a silver ion generator. With the thermal storage method processed water is kept at 160F. Heaters must be provided in all tanks and on the water lines to maintain temperature. However, a portion of the water must be cooled prior to consumption as drinking water. This cooled area of piping has proven to be a biological problem. Alternately, condensate water can be pumped at a constant rate through a silver ion generator that produces silver ions electrolytically from a silver electrode. Upon regulating the current input to the generator, silver ions are dissolved into the water at the concentration of about 200 parts per billion.(1,2)

### 1.2 Advantages of Water Chlorination

The use of water chlorination offers several important advantages over the silver ion injector approach. First, more information is known about the chlorination process and it's effects on humans than about the silver ion method. Chlorination also gives broader benefits including taste and odor control in addition to it's primary disinfecting function. Chlorination can be used to control micro-organism levels at various other stages of the water reclamation process itself. This is not practical, if at all possible, with the silver ion method. Silver ions, on the other hand, may be irreversibly consumed by the body leading to physiological changes. Also, it is difficult to maintain the silver ion residual in the presence of other chemicals in the water.

The major disadvantages to thermal storage is the power required to continuously maintain the water at 160F. This disadvantage appears most prominent when water transfer lines require trace heating and insulation.

### 1.3 Advantages of Cl<sub>2</sub>

The use of Cl<sub>2</sub> in the treatment of sanitary water is attributable to its toxicological effects on microorganisms and its oxidative capacity. In addition to its use for disinfection, it retards putrification, reduces biological O<sub>2</sub> demand, facilitates grease removal, and controls odor. Through its bactericidal action, for example, it destroys or inactivates sulfate reducing organisms that would generate odorous sulfide bearing compounds under anaerobic conditions.

- (1) Albright, C. F., Nachum, R., and Lechtman, M. D., "Development of an Electrolytic Silver-Ion Generator for Water Sterilization in Appollo Spacecraft Water Systems," Final Report, Garrett Corp., June, 1967.
- (2) Cliver, D. O., Sarles, W. B., Foell, W. K., and Goepfert, J. M., "Biocidal Effects of Silver," Wisconsin University, February, 1970.

A variety of chemicals exist that are capable of providing the disinfecting hypochlorous acid without resorting to the action of  $\text{Cl}_2$  with water. These include, for example, various forms of liquids, powders and tablets that contain calcium or sodium hypochlorite. The main drawbacks to their use have been the need for storage of a volume of potentially toxic and corrosive materials and the difficulty of feed control at the very low feed rates needed to chlorinate the small quantities of water involved (e.g., 10 pounds of water per man-day). The in-flight generation of  $\text{Cl}_2$  from common table salt (sodium chloride,  $\text{NaCl}$ ) does not have these problems.

#### 1.4 A Disinfecting System

A complete water chlorination disinfecting system includes:

1. The  $\text{Cl}_2$  supply;
2. A method of dispensing  $\text{Cl}_2$ ;
3. A method of sensing chlorination level and an electrical feedback loop to control the rate of chlorination; and
4. A method of dechlorinating water that has been given an overchlorinated, "shock" treatment.

The current program focused on the method of  $\text{Cl}_2$  supply.

#### 1.5 Safety

Although  $\text{Cl}_2$  gas is irritating to the skin, eyes and respiratory system, the current method of on-site generation avoids such dangers. The protection is simple. Chlorine is not stored but only generated as needed.

The quantity of  $\text{Cl}_2$  gas actually in existence at any time in a 12-man system would be limited to a volume of  $4 \times 10^{-6}$  cubic feet (0.1 cubic centimeter). If completely released into a confined volume of 10,000 cubic feet, the concentration of  $\text{Cl}_2$  would only be 0.04 parts per billion. This represents a much smaller risk than that associated with other methods of storing chlorination chemicals.

#### 1.6 Electrochemical $\text{Cl}_2$ Generation

The most successful attempt to an on-site approach to generation of  $\text{Cl}_2$  for space application was a program completed at the NASA Langley Research Center. (3) This activity generated  $\text{Cl}_2$  from a copper chloride solution. It identified several drawbacks to the approach that had to be solved or avoided to permit successful electrochemical generation of  $\text{Cl}_2$  for water treatment aboard a spacecraft. The identified problems included:

1. The use of copper deposition to prevent by-product  $\text{H}_2$  evolution along with  $\text{Cl}_2$  required careful current density control to prevent copper dendrites from forming. With passage of time and current such dendrite growth shorted the electrochemical cell electrodes.

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(3) Bruce, R. A., "Specialized Halogen Generator," NASA Case XLA-8913, October 9, 1969.

2. Establishing a reliable relation between current flow and  $\text{Cl}_2$  generation rate was difficult because coulometric efficiency varied. This resulted from back diffusion of a portion of the generated  $\text{Cl}_2$  through the electrolyte to the cell's cathode. Here it both chemically reacted with the copper and was electrochemically consumed.
3. An excessive amount of system complexity resulted when an AC current was used to raise the cell's operating temperature. The higher temperature was used to avoid osmotic transfer of water across the hydrophobic membrane separating the  $\text{Cl}_2$  from the water to be chlorinated.

These efforts to incorporate the best and most widely used approach to water treatment in a space environment indicated the major difficulty was developing a simple, reliable method for generating  $\text{Cl}_2$  at the time it is needed and for long periods. The on-board generating technique is necessary to avoid the need to store quantities of gaseous or liquid  $\text{Cl}_2$  within the confines of a space vehicle.

#### 1.7 Background to Current Program

As a result of its in-house search for applications of electrochemistry to aerospace applications, personnel at Life Systems constructed and demonstrated a device that permits careful control of  $\text{Cl}_2$  generation for water chlorination. It is called the CHLOROGEN device and is unique in several ways. It is applicable to small quantities of water. It allows simultaneous generation of  $\text{H}_2$  with the  $\text{Cl}_2$  but prevents any inconvenience associated with its evolution by immediately and electrochemically reacting it in an adjacent cell. The problems associated with the use of a copper cathode, therefore, are avoided.

The process is further unique in that the  $\text{H}_2$  elimination step requires no power, using ambient air as a source of the depolarizing agent for the adjacent cell couple. Direct depolarization of the  $\text{Cl}_2$  generating cell with air was not recommended since it was desired to use every method possible to separate the ambient air from the generated (0.1 cubic centimeter)  $\text{Cl}_2$ .

The CHLOROGEN device employs an electrolytic type of valve to control the flow of  $\text{Cl}_2$ . Chlorine only flows when current flows. Starting and stopping of the flow, therefore, results from the opening and closing of an electrical circuit, a process much faster in response than mechanical valves. Because of this feature, the parts per million of  $\text{Cl}_2$  required in the chlorination process can be carefully regulated. The  $\text{Cl}_2$  flowrate is directly proportional to the current flowing because each side of the electrolytic valve contains  $\text{Cl}_2$ . No other consumable material is present that can diffuse across the cell to result in coulometric inefficiencies. The total quantity of  $\text{Cl}_2$  used is accurately determined by integrating the current flow over the time interval.

Prior to initiating the current program, each one of the electrochemical components of the CHLOROGEN device had been operated as an entity--the  $\text{Cl}_2$  generator, the  $\text{H}_2$  eliminator, and the  $\text{Cl}_2$  valve.



1.8 Current Program

The purpose of the program was to build a laboratory breadboard of the Cl<sub>2</sub> generating device. The device was to be used to (a) demonstrate integrated component operation and (b) evaluate and characterize its performance. Specifically, the objectives included the following:

1. Refurbish Life Systems' existing electrochemical cell hardware and assemble it into an integrated system combining the generator, eliminator, and valve.
2. Design and fabricate test instrumentation and laboratory type controls for the device.
3. Carry out a Parametric Test Program followed by Endurance Testing.
4. Evaluate the materials of construction to identify any potential problems limiting its application.
5. Deliver the system including cell hardware.

The following sections describe the system process, hardware, and experimental results obtained on the program.

## 2.0 SYSTEM PROCESS DESCRIPTION

The process reactions occurring within the electrolytic device are based on the characteristics of three electrochemical cell couples:

1. The  $\text{Cl}_2$ -chloride ion ( $\text{Cl}^-$ ) couple;
2. The hydrogen ion ( $\text{H}^+$ )- $\text{H}_2$  couple; and
3. The  $\text{O}_2$ -water couple.

The electrochemistry of these couples are reviewed in the Appendix.

### 2.1 $\text{Cl}_2$ Generator Operation

The  $\text{Cl}_2$  required for water treatment is obtained by the electrolysis of an acid solution of  $\text{Cl}^-$  ions. The cell is composed of an anode, a cathode and the electrolyte held in a matrix. The  $\text{Cl}_2$  is formed according to the reaction



The electrochemical reaction that balances this oxidation is the reduction of  $\text{H}^+$  contained in the solution (electrolyte). The reaction is



When combined in the above arrangement, this electrochemical cell is a power consuming device with a theoretical open circuit voltage of 1.36 volts. As current is drawn, the voltage that must be imposed across the electrodes increases.

According to Faraday's Laws of Electrolysis, the quantity of  $\text{Cl}_2$  that is generated is directly proportional to the current that flows through the cell. The  $\text{Cl}_2$  generation rate can be expressed by the equation

$$W_{\text{Cl}} = 3.17 \times 10^{-2} (I)$$

where

$$W_{\text{Cl}} = \text{Cl}_2 \text{ generated, gm/day}$$

$$I = \text{current, milliamps}^{(a)}$$

The quantity of  $\text{H}_2$  that is simultaneously formed in the generation of the  $\text{Cl}_2$  can be expressed by the equation

$$W_{\text{H}} = 9.01 \times 10^{-4} (I)$$

(a) The current required would be 3.4 ma for a 12-man system with 10 lb water to be chlorinated at a 2 ppm level per man-day.

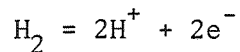
where

$W_H$  =  $H_2$  generated, gm/day

$I$  = current, milliamps

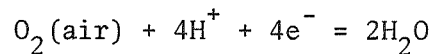
## 2.2 $H_2$ Eliminator Operation

The  $H_2$  formed during the generation of  $Cl_2$  is eliminated in an electrochemical cell.<sup>2</sup> The cell is composed of an anode, a cathode and the electrolyte held in a matrix. The  $H_2$  is consumed according to reaction



$$E_o = 0.00 \text{ v}$$

The electrochemical reaction that balances this oxidation is the reduction of  $O_2$  contained in air. The reaction is



$$E_o = 1.23 \text{ v}$$

When combined in the above arrangement, this electrochemical cell is a power generating device with a theoretical open circuit voltage of 1.23 volts.

According to Faraday's Laws of Electrolysis, the quantity of  $H_2$  that is consumed is directly proportional to the current (electrons) that flows through the cell. The  $H_2$  consumption of the eliminator can be expressed by the equation

$$W_H = 9.01 \times 10^{-4} (I)$$

where

$W_H$  =  $H_2$  consumed, gm/day

$I$  = current, milliamps

The quantity of  $O_2$  that is simultaneously consumed in the removal of the  $H_2$  can be expressed by the equation

$$W_O = 7.15 \times 10^{-3} (I)$$

where

$W_O$  =  $O_2$  consumed, gm/day

$I$  = current, milliamps

## 2.3 $Cl_2$ Valve Operation

The function of the  $Cl_2$  valve is to control the flow of pure  $Cl_2$  obtained from the generator into the water treatment diffuser. The basic valve (cell)

consists of two porous platinum electrodes separated by the electrolyte held in a porous matrix. Chlorine formed in the generator is exposed to one of the porous electrodes called the cathode. When a DC power supply is connected to the cell electrodes, electrons are caused to flow through the cathode. The  $\text{Cl}_2$  molecules (in the compartment) react with these electrons to form  $\text{Cl}^-$ . The half-cell reaction which occurs at the cathode is given by



The  $\text{Cl}^-$  migrate under the electromotive force provided by the power supply to the other porous electrode termed the anode. At this electrode the ions are discharged to again form  $\text{Cl}_2$  according to the half-reaction.



The  $\text{Cl}_2$  has now passed from the cathode compartment to the anode compartment. The electrons released at the anode travel through the external circuit back to the cathode where they react with more  $\text{Cl}_2$ . The process continues as long as  $\text{Cl}_2$  and power are provided.

According to Faraday's Laws of Electrolysis, the quantity of  $\text{Cl}_2$  that is consumed (transferred) from the generator and released in the anode compartment is directly proportional to the current that is allowed to flow through the valve. The output of the valve can be expressed by the equation

$$W_{\text{Cl}} = 3.17 \times 10^{-2} (I)$$

where

$W_{\text{Cl}}$  =  $\text{Cl}_2$  output, gm/day

$I$  = current, milliamps

Starting and stopping  $\text{Cl}_2$  flow is as simple and responsive as the opening and closing of an electrical circuit. The flowrate is directly proportional to current. The quantity is directly related to an integration of the current-time function.

### 3.0 SYSTEM HARDWARE DESCRIPTION

The laboratory breadboard of the electrolytic  $\text{Cl}_2$  generating device was divided into two units. The Cell Stand and the Control and Instrumentation Console. The two units are connected with a cable harness during system operation. Figure 1 is a photograph of the breadboard system.

#### 3.1 Cell Stand

The Cell Stand consists of the three electrochemical cells, three bubble flowmeters, wiring, electrical connectors, component supports and base plate. Figure 2 is a flow schematic of the system. The glass bubble flowmeters were specially designed to indicate and measure extremely low gas flow rates. They utilize a 10 mil orifice submerged in a liquid. The flowmeters were calibrated in bubbles per unit time for the specific gases at the operating conditions. The flowmeters are used to measure and indicate  $\text{H}_2$  and  $\text{Cl}_2$  flows between and out of the cells.

When the flowmeter is used in the cathode feed of the  $\text{H}_2$  eliminator, pressurized air or  $\text{O}_2$  is needed to overcome the pressure drop of the meter and manifold of the cathode compartment. Hardware is available to measure the temperature of each cell with a sheathed thermocouple probe. The wires from the voltage leads, current leads and thermocouples from the electrochemical cells terminate in multi-pin connectors mounted onto the base of the stand. This base and all component supports were fabricated from acrylic plastic. Flexible vinyl tubing and polypropylene fittings are used to carry the system's process fluids.

A blower is available for supplying air or  $\text{O}_2$  to the cathode of the eliminator. To use it, however, would require incorporating slots into the cell endplates to lower the pressure drop experienced when the air flows through the cell.

The following sections discuss the cells in more detail.

##### 3.1.1 $\text{Cl}_2$ Generator

The function of the generator is to electrochemically generate gaseous  $\text{Cl}_2$  from the  $\text{Cl}^-$  contained in the acidic electrolyte. Figure 3 shows a cross-section of the cell used. It consists of three internal compartments. The center compartment contains the electrolyte. The anode compartment contains the generated  $\text{Cl}_2$  gas. The cathode compartment collects the by-product  $\text{H}_2$ . Each gas compartment is separated from the bulk electrolyte by a porous matrix sandwiched between a porous electrode and a plastic screen.

Table 1 summarizes the materials of construction used and other characteristics of the generator. This cell can be mounted with its long axis in a vertical or horizontal plane. If a flowing electrolyte mode of operation is used, the vertical orientation is preferred. At the 5 amperes per square foot (ASF) level, the 3 square inches of active cell electrodes are able to produce enough  $\text{Cl}_2$  to disinfect drinking water for a crew of 120 men at the 2 ppm chlorination level and 30 pounds of water per man-day. This cell size was used in the breadboard to allow use of existing cell hardware.

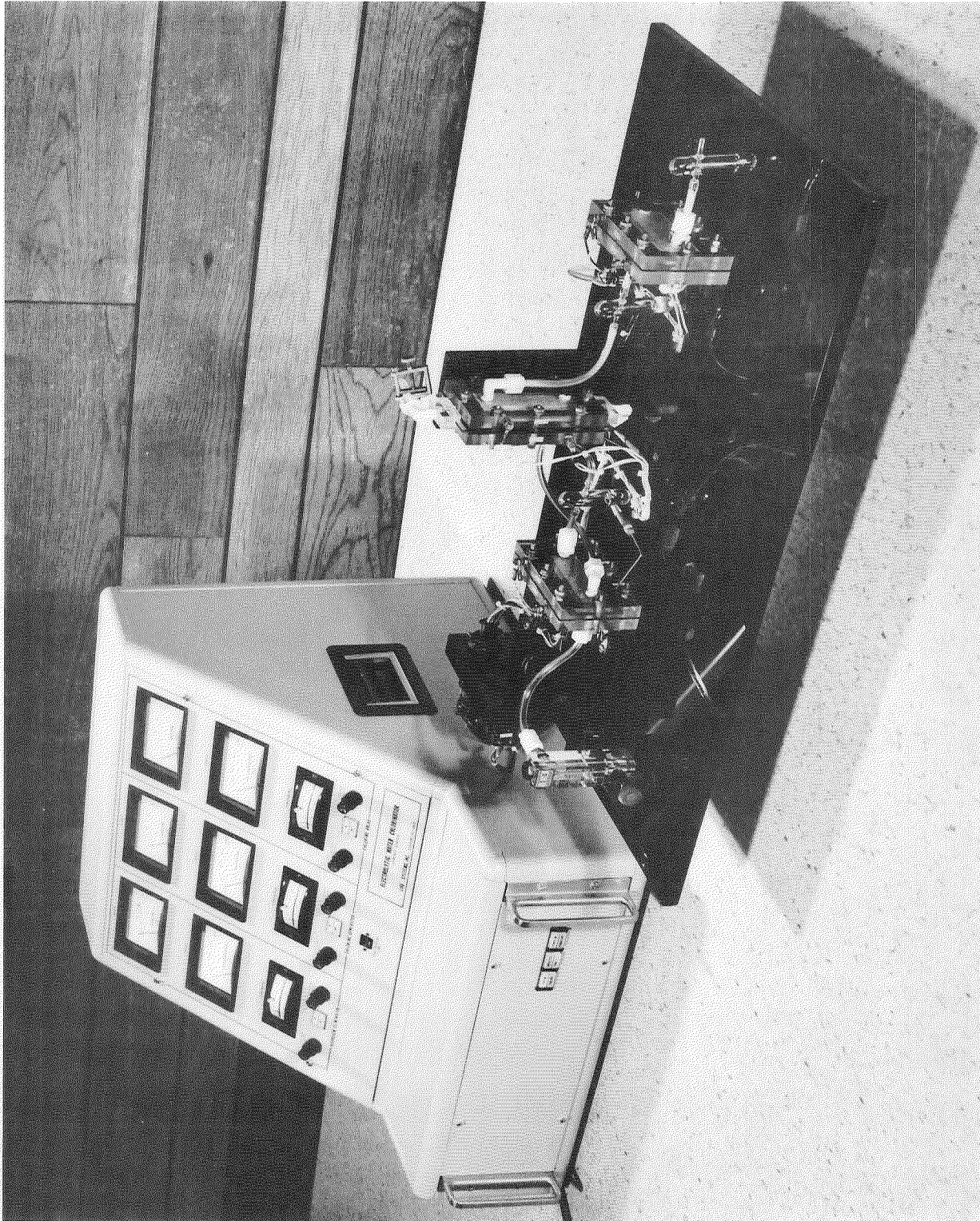


FIGURE 1    LABORATORY BREADBOARD SYSTEM

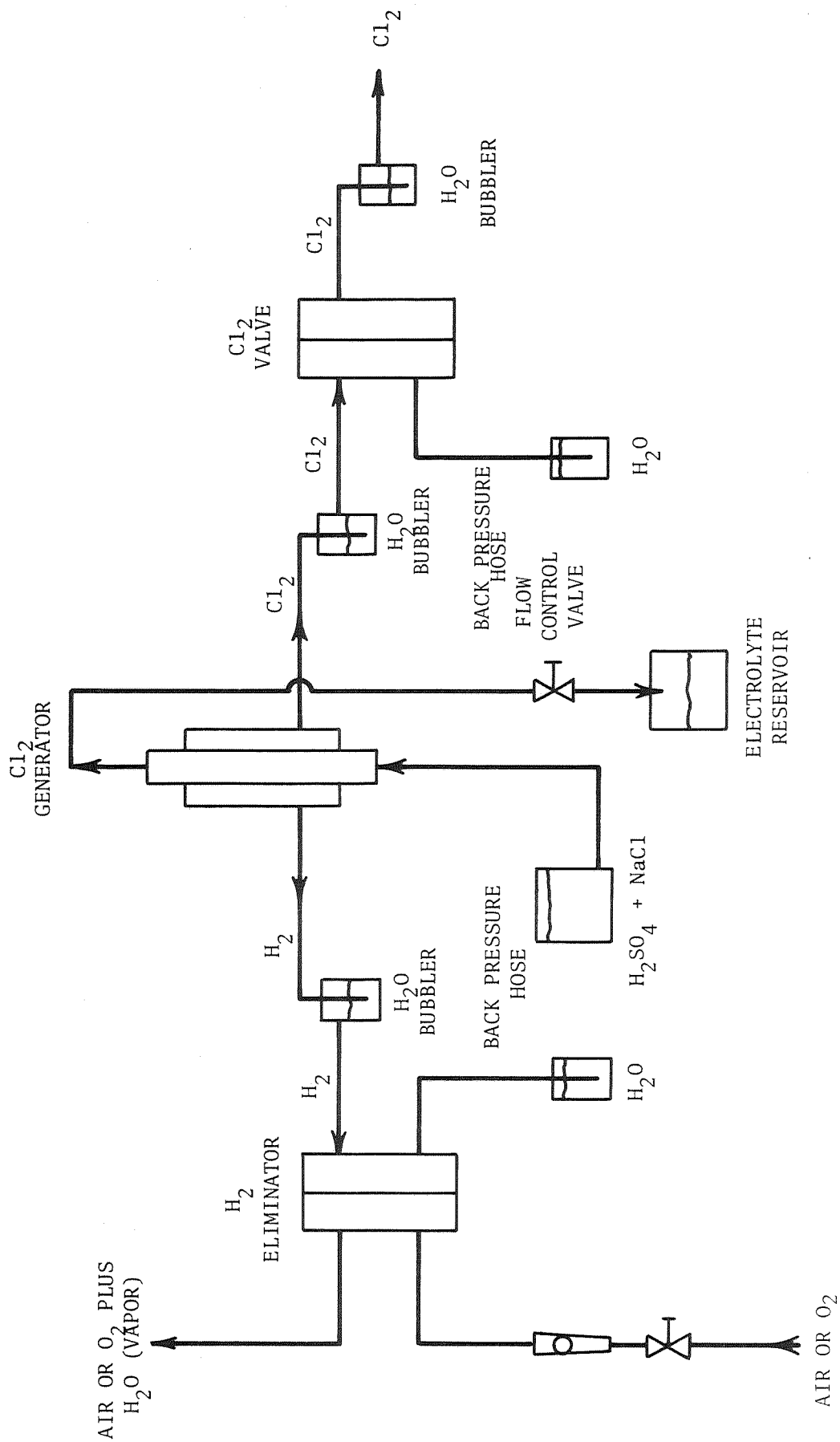


FIGURE 2 LABORATORY BREADBOARD SYSTEM FLOW SCHEMATIC

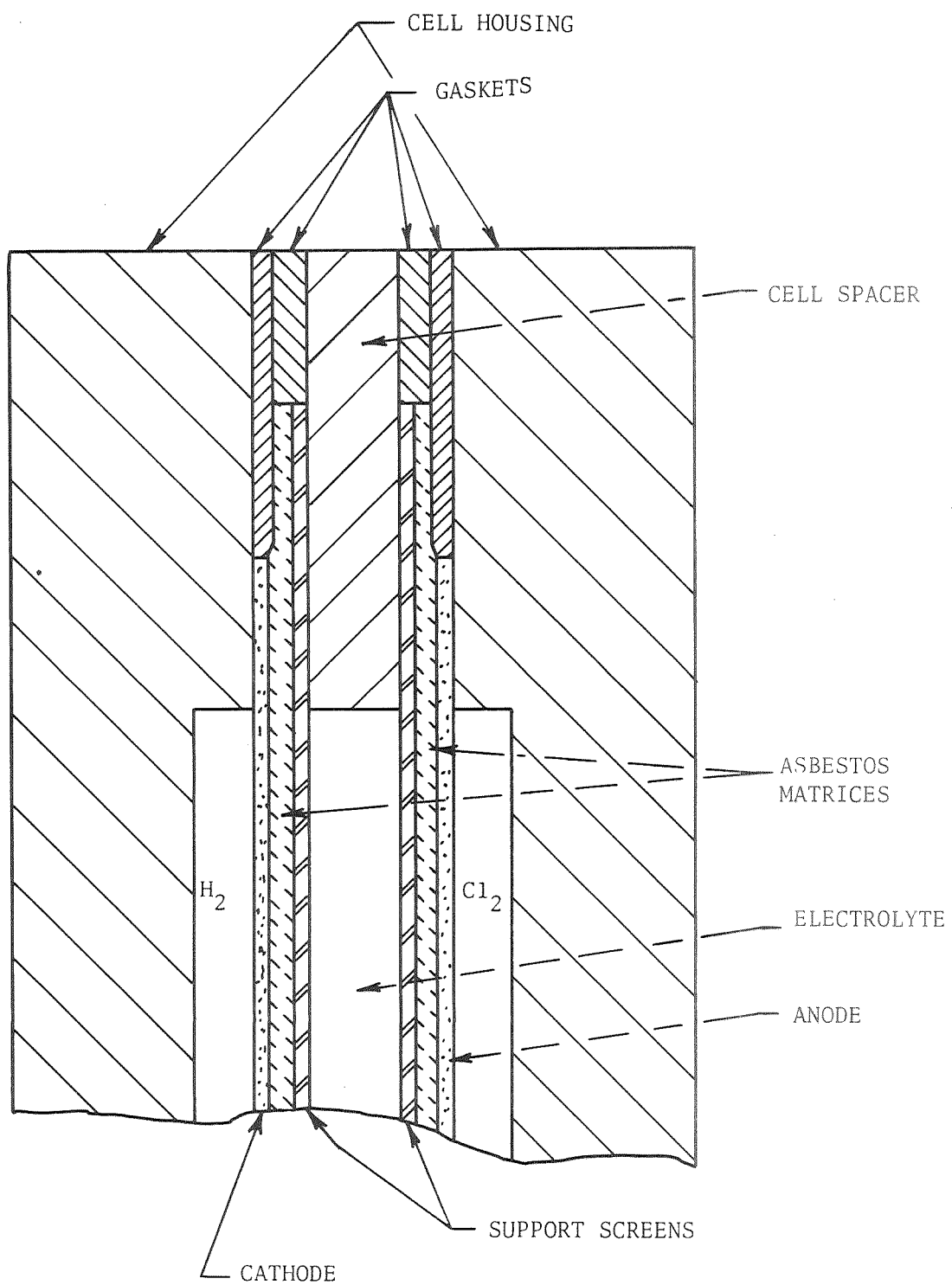


FIGURE 3  $\text{Cl}_2$  GENERATOR CELL



TABLE 1 CELL CHARACTERISTICS AND MATERIALS

	H <sub>2</sub> Eliminator	Cl <sub>2</sub> Generator	Cl <sub>2</sub> Valve
Active Area	1 x 3 inch	1 x 3 inch	1 x 3 inch
Overall Cell Dimensions	5 x 3 x 1 inch	6.5 x 3 x 1.2 inch	5 x 3 x 1 inch
Electrolyte	25% H <sub>2</sub> SO <sub>4</sub>	25% H <sub>2</sub> SO <sub>4</sub> Sat. with NaCl	25% H <sub>2</sub> SO <sub>4</sub> Sat. with NaCl
Cell Housing	Cast Acrylic	Cast Acrylic	Cast Acrylic
Cavity Spacer Screens	12-Mesh Polypropylene	12-Mesh Polypropylene	12-Mesh Polypropylene
Matrix Support Screens	70-Mesh Polypropylene	70-Mesh Polypropylene	70-Mesh Polypropylene
Matrices	20-Mil Blue Asbestos (Quebec Fiber)	20-Mil Blue Asbestos (Quebec Fiber)	20-Mil Blue Asbestos (Quebec Fiber)
Gaskets	Viton (1/32 & 1/64 inch thick)	Viton (1/32 & 1/64 inch thick)	Viton (1/32 & 1/64 inch thick)
Electrodes	Pt Black on Pt Screen	Pt Black on Pt Screen	Pt Black on Pt Screen
Electrode Positioning Tape	3.5 Mil Teflon Tape	3.5 Mil Teflon Tape	3.5 Mil Teflon Tape

### 3.1.2 H<sub>2</sub> Eliminator

The function of the eliminator is to consume the by-product H<sub>2</sub> from the generator. The eliminator acts as a power generating device having gas compartments separated by a porous matrix sandwiched between porous electrodes. Hydrogen enters the anode side of the cell while the cathode side is exposed to air or O<sub>2</sub>. Oxygen and H<sub>2</sub> are consumed to form negligible amounts of electrical power, heat and water. Figure 4 shows a cross-section of the eliminator. Table 1 summarizes the cell's characteristics.

### 3.1.3 Cl<sub>2</sub> Valve

The function of the electrolytic valve is to accurately meter the Cl<sub>2</sub> gas prior to dispersing it into water. It is identical in construction to the eliminator. (See Figure 4 and Table 1.)

## 3.2 Control and Instrumentation Console

This console houses all of the controls and instrumentation required to operate and monitor individual cell or integrated system operation. It contains three identical, direct current power supplies with an output range of 0-10 VDC and 0-2 amperes. The power supplies are of the automatic crossover type enabling constant current or constant voltage operation.

The constant current control results in a constant gas generation rate. The constant voltage feature can be used to set a maximum cell-voltage limit.

Each cell can be operated with its own power supply or all three cells can be operated electrically in series using only one power supply. The operating mode is selected by actuating a single switch located on the front panel. Since the eliminator is a power producing device, the power supply acts as a zero resistance load. Parametric testing operation is more easily carried out in this manner since cell voltage output fluctuations do not affect current flow (gas generation rates) as occurs with a simple resistance as the load. Fine and coarse current and voltage adjust knobs for the power supplies were mounted onto the front panel of the console. These control knobs, together with the switch for selecting one common or three individual power supplies, individual ON-OFF switches for each power supply, one power ON-OFF switch and one fan ON-OFF switch comprise the controls for the system.

All system instrumentation is mounted on an inclined front panel of the console. It consists of three 0-5 VDC voltmeters, three 0-1000 milliampere ammeters, three 0-300F pyrometers and one, non-resettable total operating time indicator set to read in hours.

All electrical connections for system power and instrumentation are made in back of the console via two connectors and one thermocouple strip-panel. The console is protected by a 3 ampere resettable circuit breaker. All switches are of the illuminated pushbutton type.

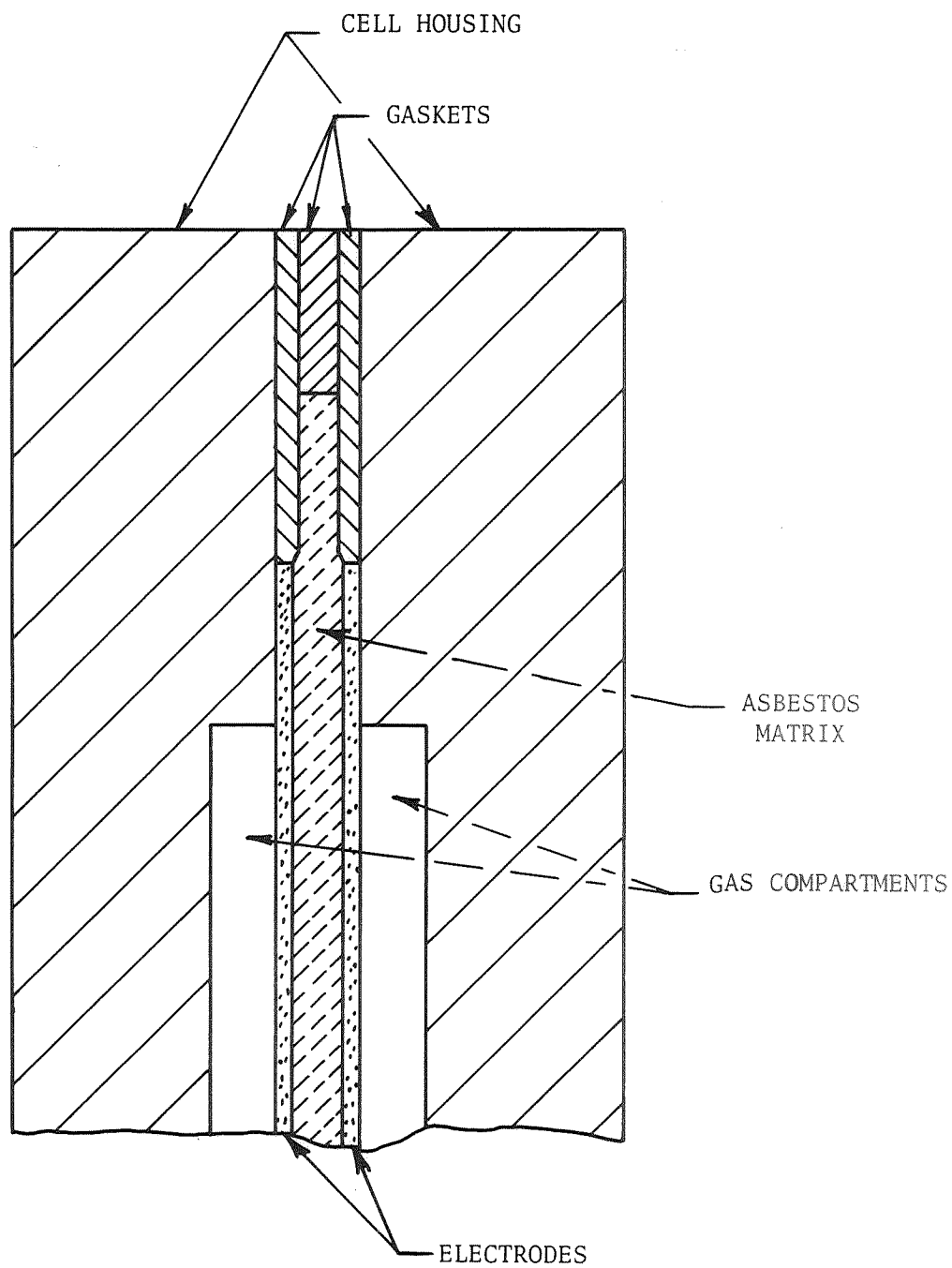


FIGURE 4 H<sub>2</sub> ELIMINATOR/Cl<sub>2</sub> VALVE CELL

Maintainability was a prime consideration in designing the console. By using electrical connectors, the console can be quickly disassembled into four sub-assemblies; the front panel, power supply rack, connector panel, and console enclosure. Two separate and detachable connecting cables are used to supply power to the console and connect the cell stand with the console. Quick accessibility to console components is provided through a rear panel door.

#### 4.0 SYSTEM OPERATION

##### 4.1 Short-Term Operation

The laboratory breadboard was designed to demonstrate integrated component operation. It was therefore limited to a short-term, continuous operating time capability. After integrated operation was successfully demonstrated and characterized, and with a slight modification, long-term operating times were able to be achieved. In the short-term mode the center compartment of the generator is filled with sodium chloride (NaCl) saturated, 25% sulfuric acid ( $H_2SO_4$ ). The number of dissolved  $Cl^-$  contained in this volume of electrolyte was sufficient for approximately 4 hours of system operation at 5 ASF.

##### 4.2 Endurance Operation

For extended operating times, a flow of electrolyte is allowed to pass slowly through the center compartment of the generator. This is achieved in a gravity environment by using two electrolyte containers at different elevations. Both containers were lower than the cell elevation. With the three cells charged with electrolyte and mounted on the Cell Stand, power is applied to the system from the Control and Instrumentation Console.

##### 4.3 Power Supply Selection

With the mode selector switch in the "Three P.S." position, any one, two, or three cells can be operated by pushing the individual ON-OFF cell switches. Current and voltage levels are individually controlled for each cell. With the mode selector switch in the "Single P.S." position, the cell ON-OFF switches are taken out of the circuits and the current and voltage controls for the  $H_2$  eliminator power supply are used to control the breadboard's current and voltage.

##### 4.4 System Start-Up

Typical start-up is achieved by using the "Three P.S." mode and applying power first to the generator. The other two cells are in the unpowered condition. With current flowing through the generator, gases start to bubble through the bubble flowmeters on either side of this cell. These gases are allowed to flow through the gas inlet sides of the other two cells, and out through the backpressure hoses, thus flushing out residual gases in these compartments. After several minutes of flushing, power can also be applied to these cells. Once all three cells are operating, either "Three P.S." or "Single P.S." operation can be used. If desired, and by observing the liquid levels in the backpressure hoses, a variety of system operating conditions can be set up by manipulating the current levels.

## 5.0 EXPERIMENTAL RESULTS

The primary objective of the test program was to demonstrate integrated system operation preceeded by minimum individual cell parametric testing. The experimental program was divided into six parts. They were:

1. Electrolyte composition selection
2. Individual cell performance characterization
3. Integrated system characterization
4. Gas purity
5. Integrated system endurance testing
6. Material evaluation

### 5.1 Electrolyte Composition Selection

In-house studies had shown that  $\text{H}_2\text{SO}_4$  containing dissolved NaCl was a suitable electrolyte for both generator and valve while  $\text{H}_2\text{SO}_4$  was found suitable for the eliminator. Further analytical and experimental studies were conducted to determine optimum electrolyte composition and concentration for the three cells. Taken into account were moisture balance between individual cells and the environment, electrolyte conductivity values, and solubility of NaCl, the source of  $\text{Cl}^-$ .

For an ambient dew point range of 50 to 70F the optimum electrolyte concentration for the eliminator was found to be 25%  $\text{H}_2\text{SO}_4$  by weight. The cell was designed to tolerate the volume changes resulting from this range in dew point variation. The electrolyte composition and concentration selected for the generator and valve was 25%  $\text{H}_2\text{SO}_4$  saturated with NaCl.

The solubility of NaCl in 25%  $\text{H}_2\text{SO}_4$  was experimentally found to be 20 grams per 100 ml of 25%  $\text{H}_2\text{SO}_4$  at 75 F.

### 5.2 Individual Cell Performance

The electrochemical performance of the generator, valve and eliminator were experimentally determined. The results are presented in Figures 5 through 7, respectively. The performances are also compared to data originally obtained with slightly different cell hardware and operating conditions. Pertinent data for both curves are indicated on each figure. Diference in cell construction and, where applicable, in operating conditions account for the minor differences in the data. Both sets of data for the three cells, however, fall within expected ranges of performance as indicated by the voltage levels.

### 5.3 Integrated System Characterization

The results of the system's electrochemical performance are shown in Figure 8. The data compares favorably with that obtained with the cells individually operated. The figure shows that at a current density of approximately 40 ASF the  $\text{Cl}_2$  generator voltage started to rise rapidly, indicating start of a new

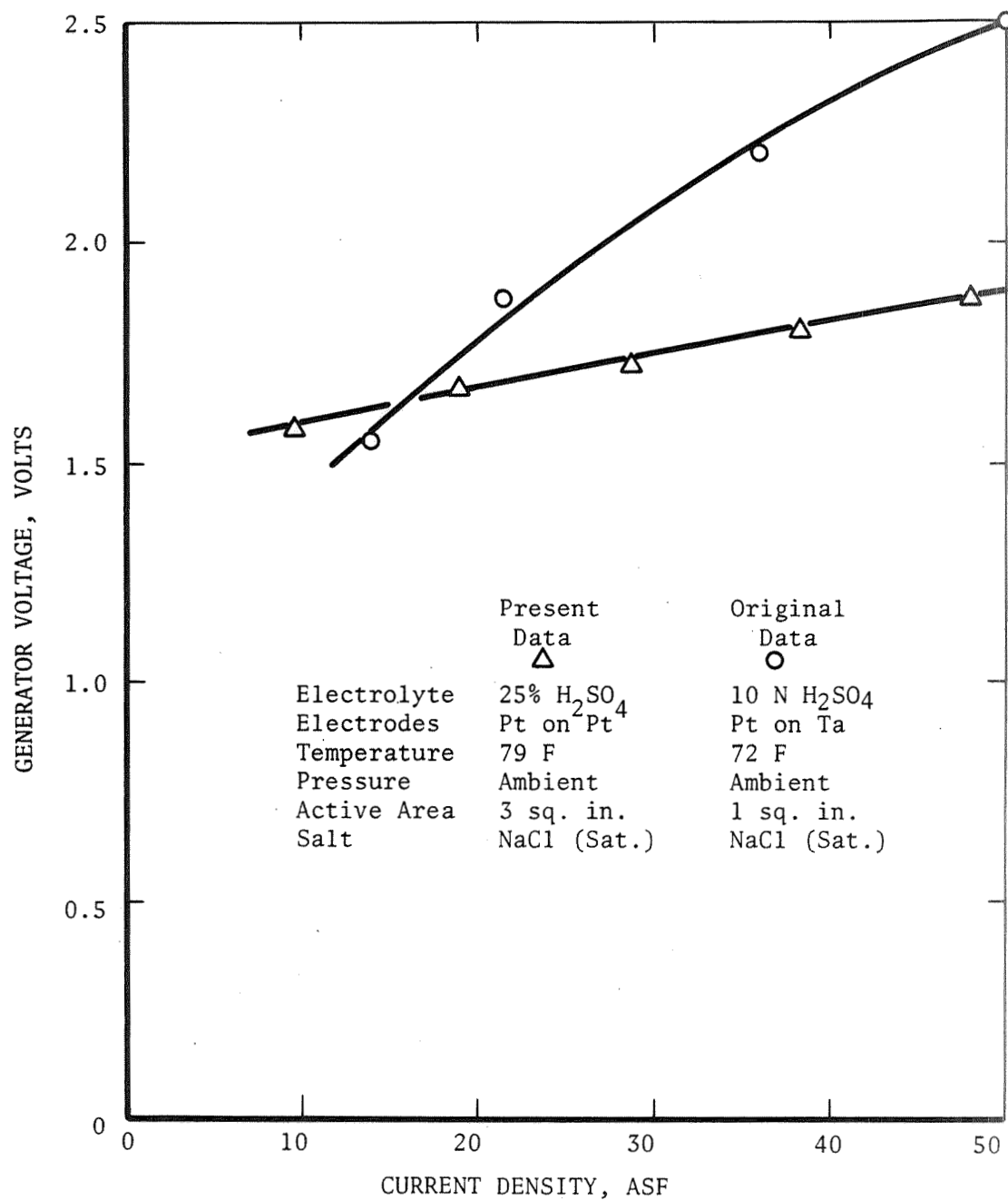


FIGURE 5 Cl<sub>2</sub> GENERATOR PERFORMANCE

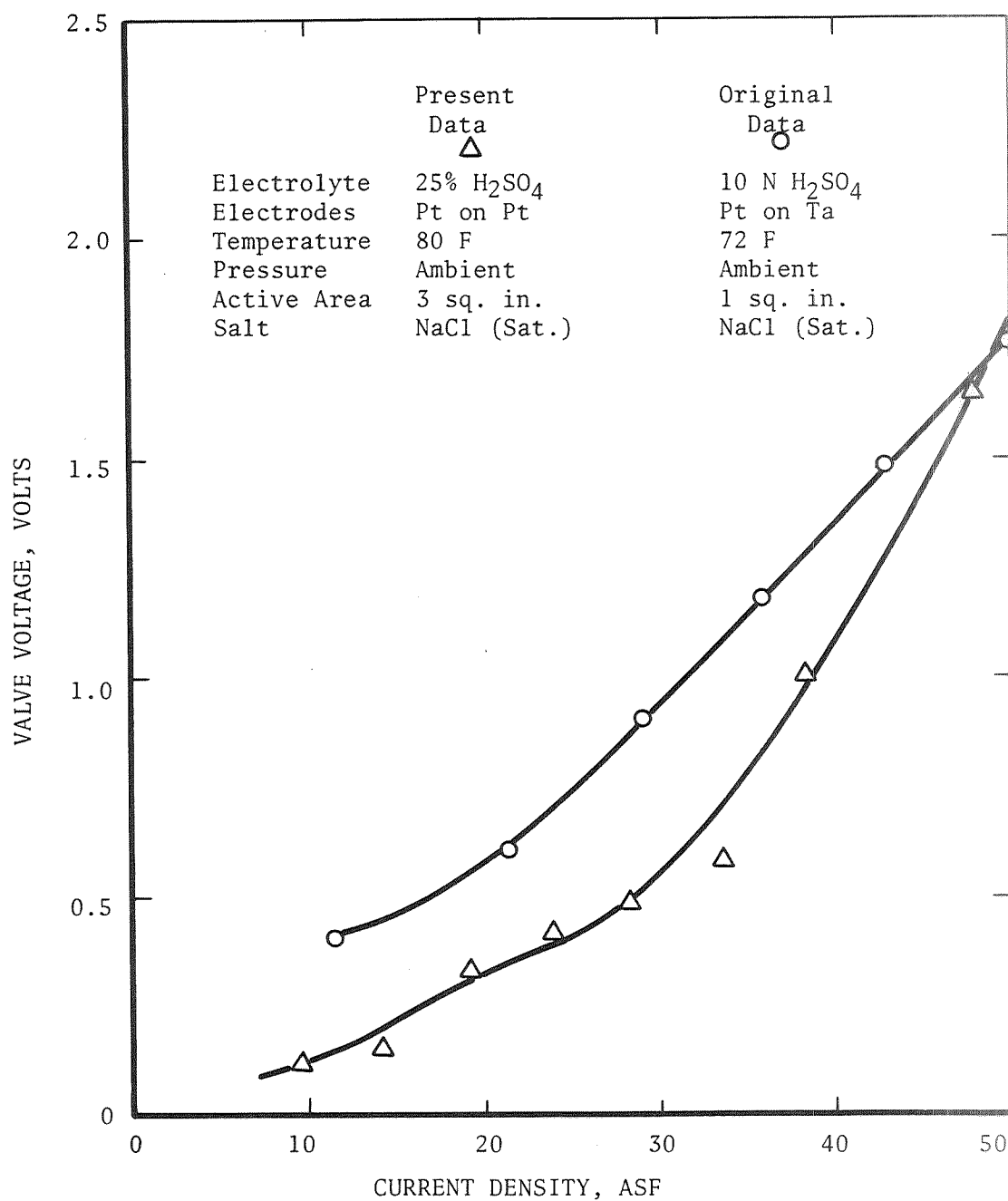


FIGURE 6 Cl<sub>2</sub> VALVE PERFORMANCE



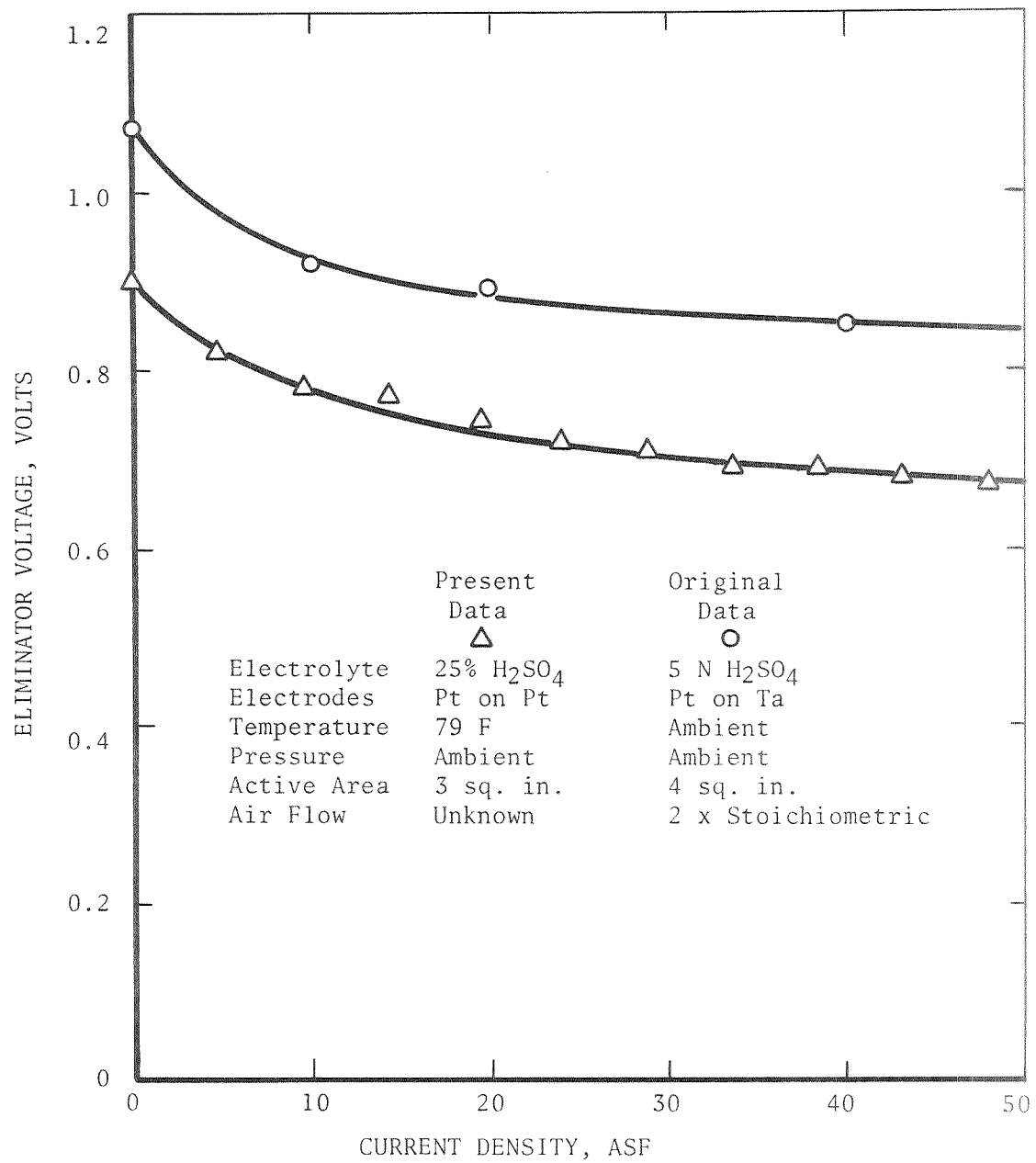
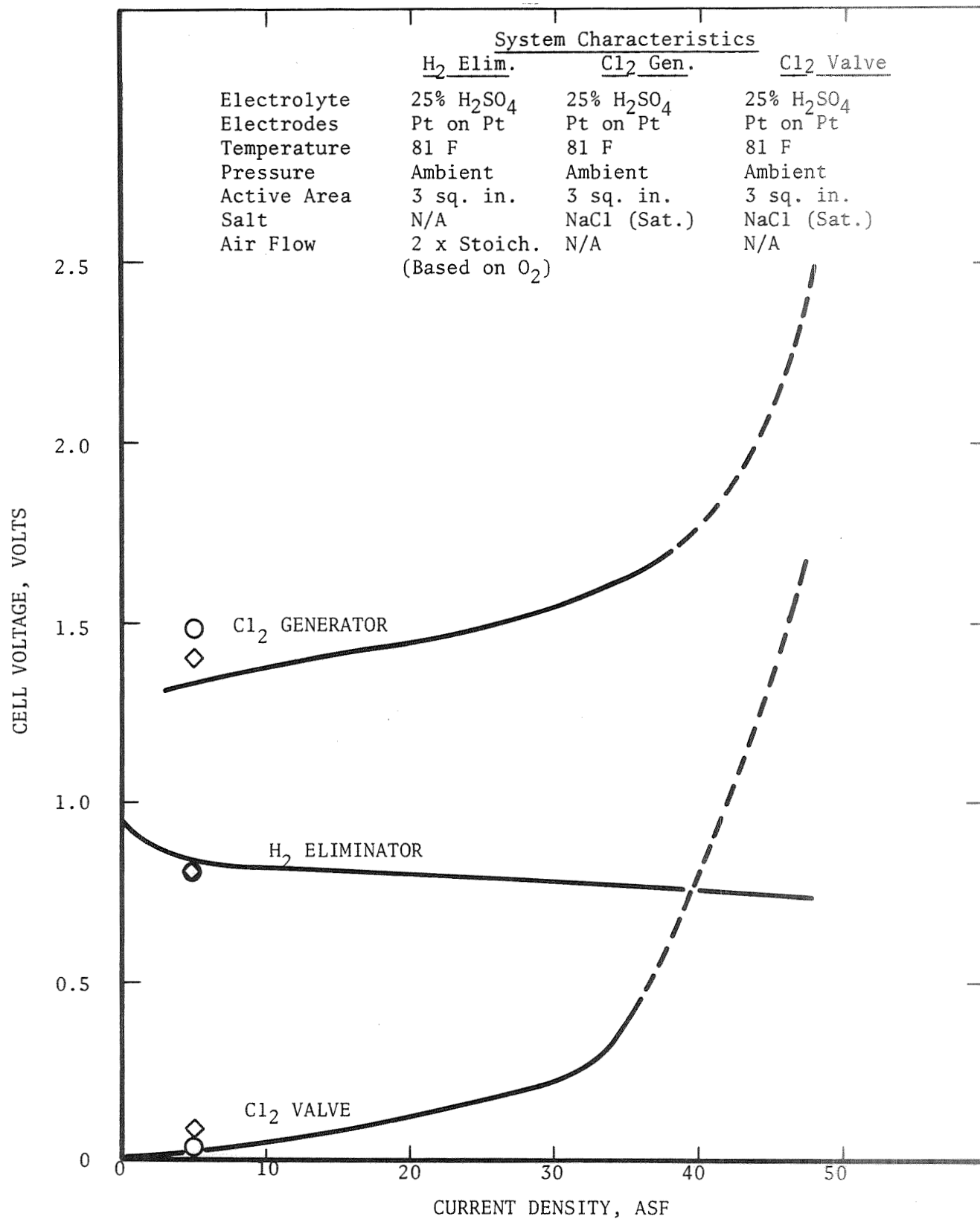


FIGURE 7 H<sub>2</sub> ELIMINATOR PERFORMANCE



- ◇ SYSTEM PERFORMANCE AFTER 250 HOURS OF OPERATION
- SYSTEM PERFORMANCE AFTER 788 HOURS OF OPERATION

FIGURE 8 INTEGRATED SYSTEM PERFORMANCE CHARACTERISTICS

$\text{Cl}_2$  evolution mechanism coupled, possibly, with  $\text{O}_2$  evolution. The occurrence of some  $\text{O}_2$  evolution could account for the simultaneous rise in valve voltage as shown in the data. These results further support the selection of low current density operation for prototype hardware.

System operation was unaffected by pressure differentials of  $\pm 3$  inches of water. The system was operated over the ambient temperature range of 73 to 83F at ambient pressure. No change in performance was observed as a result of the temperature variations. Also indicated on Figure 8 are the performance levels of the three cells after 250 and 788 hours of operation at 5 ASF. This data was obtained during and at the completion of the endurance testing described below.

#### 5.4 Gas Purity

Three methods were used to establish purities of the generated gases--chemical analysis, volumetric analysis, and electrochemical coulometric analysis.

##### 5.4.1 Chemical Analysis

A chemical analysis was made of the  $\text{H}_2$  and  $\text{Cl}_2$  evolved from the generator and the  $\text{Cl}_2$  vented from the valve.

The  $\text{H}_2$  gas from the generator was bubbled through 100 ml of distilled water for 24 hours. The water was then analyzed to determine if any  $\text{Cl}_2$  gas had been present in the  $\text{H}_2$ . The standard Orthotolidine method for total available  $\text{Cl}_2$ , both free and combined available, was used.<sup>(4)</sup> No  $\text{Cl}_2$  was detected. The test was sensitive to 0.03 ppm. The  $\text{H}_2$  was also given a smell test. No  $\text{Cl}_2$  odor was noted. Typically, one can detect the presence of 2 to 4 ppm of  $\text{Cl}_2$  in a gas.

The same Orthotolidine method was used to quantitatively measure outputs of  $\text{Cl}_2$  from both the generator and the valve. Chlorine from the cell was again allowed to diffuse into a known quantity of distilled water for a given period of time. The water was then analyzed for free and combined available  $\text{Cl}_2$ . A  $\text{Cl}_2$  level of 1.50 ppm was measured during the generator test. This compared to a calculated or theoretical value of 1.54 ppm based on the current passed. This reflects a gas purity of 98%. For the  $\text{Cl}_2$  valve the measured value was 1.00 ppm compared to a calculated level of 1.06 ppm. The purity reflected was 95%. This is a difficult experiment to carry out accurately because of the small quantities of gas involved and the relatively large gas line volumes of the laboratory breadboard. Experimental accuracy was only felt to be  $\pm 5\%$  compared with the better than 1% accuracy for the test on the  $\text{H}_2$  carried out over a 24-hour period.

##### 5.4.2 Volumetric Analysis

A volumetric analysis was made on the  $\text{H}_2$  evolved from the generator and the  $\text{Cl}_2$  evolved from the valve. The volumetric flowrate measurements were made by timing the movement of a liquid segment inside a 0.114 inch inside diameter precision glass tube.

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(4) "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, Inc., 12th Ed., 1965.

The theoretical  $H_2$  evolution rate calculated on the basis of current flowing was 0.820 cubic centimeters per minute (cc/min). The measured flowrate was 0.827 cc/min. The purity calculated is 101%. Since the accuracy of the instrumentation was limited to  $\pm 1\%$ , the purity of  $H_2$  gas was concluded to be 100%.

The calculated flowrate of the  $Cl_2$  valve was 0.770 cc/min based on the current level. The measured value was 0.720 cc/min. The calculated purity is 94%. Again, the carrying out of the experiment with  $Cl_2$  was sensitive due to the high solubility of  $Cl_2$  in the flow indicating liquid section. Hydrogen solubility in the liquid was negligible and caused no complication since once the liquid was saturated, small changes in room temperature and pressure had no effect on the quantity of  $H_2$  being passed through the flowmeter.

#### 5.4.3 Electrochemical Analysis

Probably the most accurate method for determining the purity of the gases generated is an electrochemical operational balance. This is especially true where  $Cl_2$  is involved. The same holds true for  $H_2$ , but the need is not as great since the other methods used had shown the  $H_2$  purity to be 100%.

With the electrochemical process, the  $Cl_2$  generated was passed into the  $Cl_2$  valve immediately after venting from the generator's anode compartment. Once in the valve and with the current flowing, the  $Cl_2$  was immediately consumed. If any  $O_2$  were formed simultaneously with the  $Cl_2$  it would have appeared by an increase in the level of the valve's voltage. The electrochemical consumption of  $O_2$  under the conditions of the experiment required considerably more voltage (i.e., 0.5 volt versus 0.02 volts at the 5 ASF level). Over many hours of operation, including that of the endurance test itself, the valve voltage remained in the region where only  $Cl_2$  could be consumed. No indication of fall-off in valve performance (increase in operating voltage) was observed which could be attributed to the presence of  $O_2$  with the  $Cl_2$ .

From the above analyses it can be concluded that the  $H_2$  is generated free of any  $Cl_2$ . The  $Cl_2$  is generated free of any  $O_2$  and, since the coulometric balance performed on the  $H_2$  indicated that 100% was being exhausted from the  $H_2$  compartment, no  $H_2$  was being transferred to the  $Cl_2$  compartment.

#### 5.5 Integrated System Endurance Testing

After completion of the system's performance characterization, the endurance test program was initiated. The operating conditions selected were a current density of 5 ASF and ambient temperature and pressure. Electrolyte was allowed to flow at approximately 100 drops per minute through the center compartment of the generator. This was sufficient to maintain constant  $Cl^-$  and  $H^+$  concentrations. The goal of the endurance testing for the integrated system was 168 hours. Actual total operating time was 788 hours or 33 days. The test was then terminated to allow time for materials evaluation prior to program completion. Figure 9 shows cell voltage versus operating time for the 788 hours. The voltage fluctuations during the initial 100 hours of operation were a result of learning how to set the electrolyte flow so no stoppage would occur during overnight operation. A redesign of the flow controller and manual adjustments in flow restrictions solved this problem.

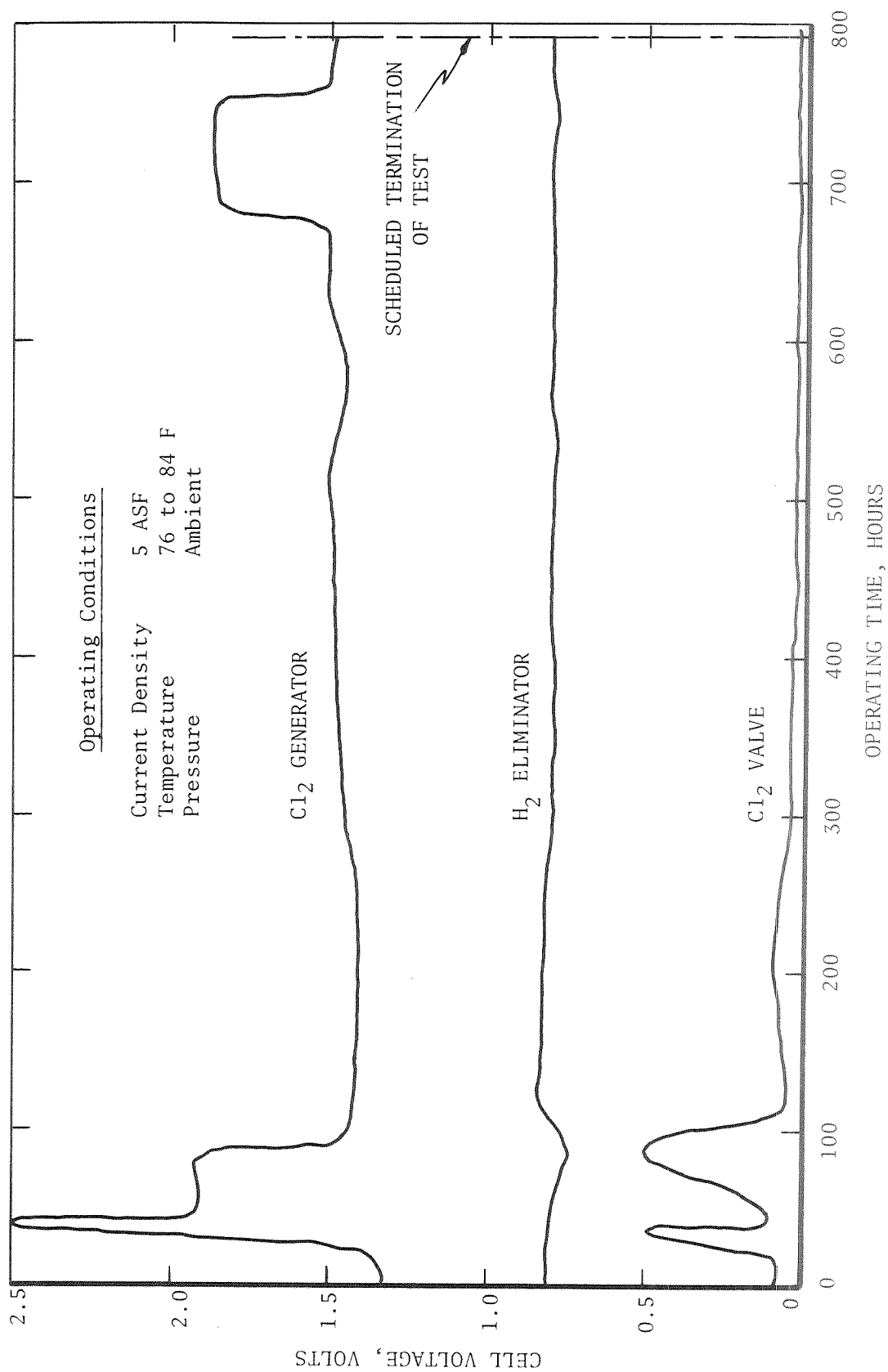


FIGURE 9 SYSTEM PERFORMANCE AS A FUNCTION OF TIME

The cause of the increase in the generator voltage from 1.5 to 1.85 volts that occurred near 675 hours of operation is not known. It could have been a change in the mechanism of  $\text{Cl}_2$  evolution resulting from a change in the electrode surface properties (e.g., electrode poisoning). This theory is supported by (a) observing that the voltage remained constant for more than 50 hours at the new level of 1.85 volts, (b) the valve voltage remained constant indicating no  $\text{O}_2$  was simultaneously being generated with the  $\text{Cl}_2$  to build up in concentration in the valve's gas compartment, and (c) a 1 second interruption in current at 750 hours caused a sudden drop in the generator voltage from 1.85 to 1.5 volts where it remained until the scheduled test termination point was exceeded.

#### 5.6 Material Evaluation

After termination of the endurance testing the three cells were disassembled for evaluation of material (see Table 1) compatibilities to the operating environments.

None of the components showed any visible signs of deterioration after the 788 hours of integrated system operation except the  $\text{Cl}_2$  electrodes. The  $\text{Cl}_2$  electrodes showed partial loss of the platinum black. Visual examination with a 20 power magnification microscope indicated that the platinum screen support, however, was not undergoing the dissolution found with the high surface area black. The anode of the generator showed an estimated loss of approximately 50% of its original platinum black. The anode and cathode of the valve showed losses of approximately 80 and 90%, respectively. It appears that the high surface platinum black was dissolved into the electrolyte. Selection of improved electrodes being evaluated under in-house activities appear to resolve the platinum black dissolution question.

6.0 DESIGN RECOMMENDATIONS

6.1 Materials

The results of the material evaluations indicated that the materials selected were suitable for the cells of the electrolytic chlorinator. Selection of a modified  $\text{Cl}_2$  electrode will completely safeguard against the gradual, and long-term dissolving of platinum black.

6.2 Configuration and Sizing

The next generation of the electrolytic chlorinator should be designed and sized to meet specific criteria; for example, a six-man, 180-day requirement. Such a design would need an appreciable decrease in active cell area even when using the recommended low current density level of 5 ASF. The cells should use a common cell housing. The flow bubblers should be eliminated and shared gas compartments interconnected directly, e.g., the cathode compartment of the  $\text{Cl}_2$  generator can also serve as the anode compartment of the eliminator, while the anode compartment of the generator can be identical to the cathode compartment of the valve. Electrolyte storage and flow regulation,  $\text{Cl}_2$  dispersion and automatic chlorination level sensing and control represent recommended additions to the next generation water disinfecting system development.

7.0 CONCLUSIONS

The following conclusions can be drawn based on the work performed under this contract:

1. Integrated operation of the three-cell, electrolytic chlorinator was successful and performed as predicted.
2. Extended operating times are possible with more than 30 days having been demonstrated.
3. Materials of construction are available for operating times exceeding 180 days.



## APPENDIX

### DISCUSSION OF REDUCTION POTENTIALS

#### A.1 Cl<sub>2</sub> - Cl<sup>-</sup> Couple

The best value for the potential for the Cl<sub>2</sub>-Cl<sup>-</sup> couple is that obtained from the cell measurements of this electrode against the AgCl-Ag electrode,



Because of the "hydrolysis" of Cl<sub>2</sub> and the formation of hypochlorite, the potential becomes meaningless in alkaline solutions.

The couple is reversible and Cl<sub>2</sub> is a rapid oxidizing agent. In this respect, it is a stronger oxidizing agent than O<sub>2</sub>. Because of the mechanism of the formation of the Cl<sub>2</sub> molecule by oxidation of the Cl<sup>-</sup>, overvoltages exist. At approximately 100 ASF this value is 0.026 volt for a platinized platinum and 0.054 for smooth platinum. Chlorine evolution is complicated by the fact that the oxidation potential of water is lower than that of Cl<sub>2</sub>; hence, were it not for the typically high O<sub>2</sub> overvoltage, no Cl<sub>2</sub> would be evolved by the electrolysis of chloride solution at low current densities.

Chlorine is stable in acid solutions with respect to disproportionation, but the reaction does have a measurable equilibrium. It is unstable with respect to the evolution of O<sub>2</sub> and Cl<sub>2</sub> solutions do slowly oxidize water which contribute to its water treatment effectiveness.

#### A.2 H<sup>+</sup>-H<sub>2</sub> Couple

The H<sup>+</sup>-H<sub>2</sub> couple is one of the best known couples. It serves as the standard reference electrode and its potential has been arbitrarily set at zero:



#### A.3 O<sub>2</sub>-Water Couple

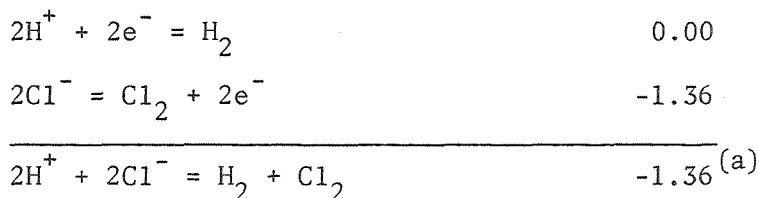
Based on the heat of formation and the entropy of formation of water, the O<sub>2</sub> couple in acid solution is



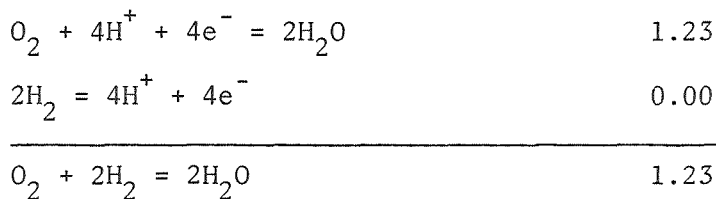
This potential has the same importance in reference to the stability of oxidizing agents in water solution that those for H<sub>2</sub> have to the stability of reducing agents. Thus, the oxidized form of any couple with a more positive potential than O<sub>2</sub>, at a given concentration of H<sup>+</sup>, should liberate O<sub>2</sub> from the solution. The O<sub>2</sub> couple is highly irreversible and, in general, it is impossible to experimentally obtain reversible performance.

Figure A-1 summarizes the relationships between the various reduction potentials. It also indicates the changes in potential that occur when current is drawn through an electrode at which the various indicated oxidation or reduction reaction is occurring. Finally, the figure indicates the combinations of reactions that result in Cl<sub>2</sub> generation, H<sub>2</sub> oxidation (elimination of H<sub>2</sub> gas) and Cl<sub>2</sub> metering:

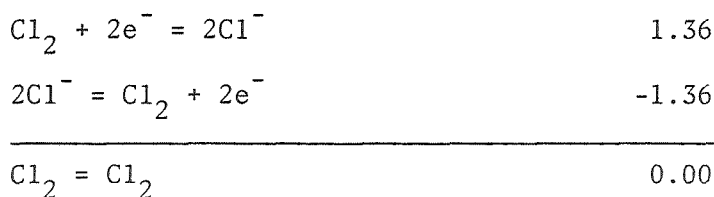
1. Chlorine Generation



2. Hydrogen Elimination



3. Chlorine Metering



(a) If the value is negative, power is required. If the value is positive, power is generated.

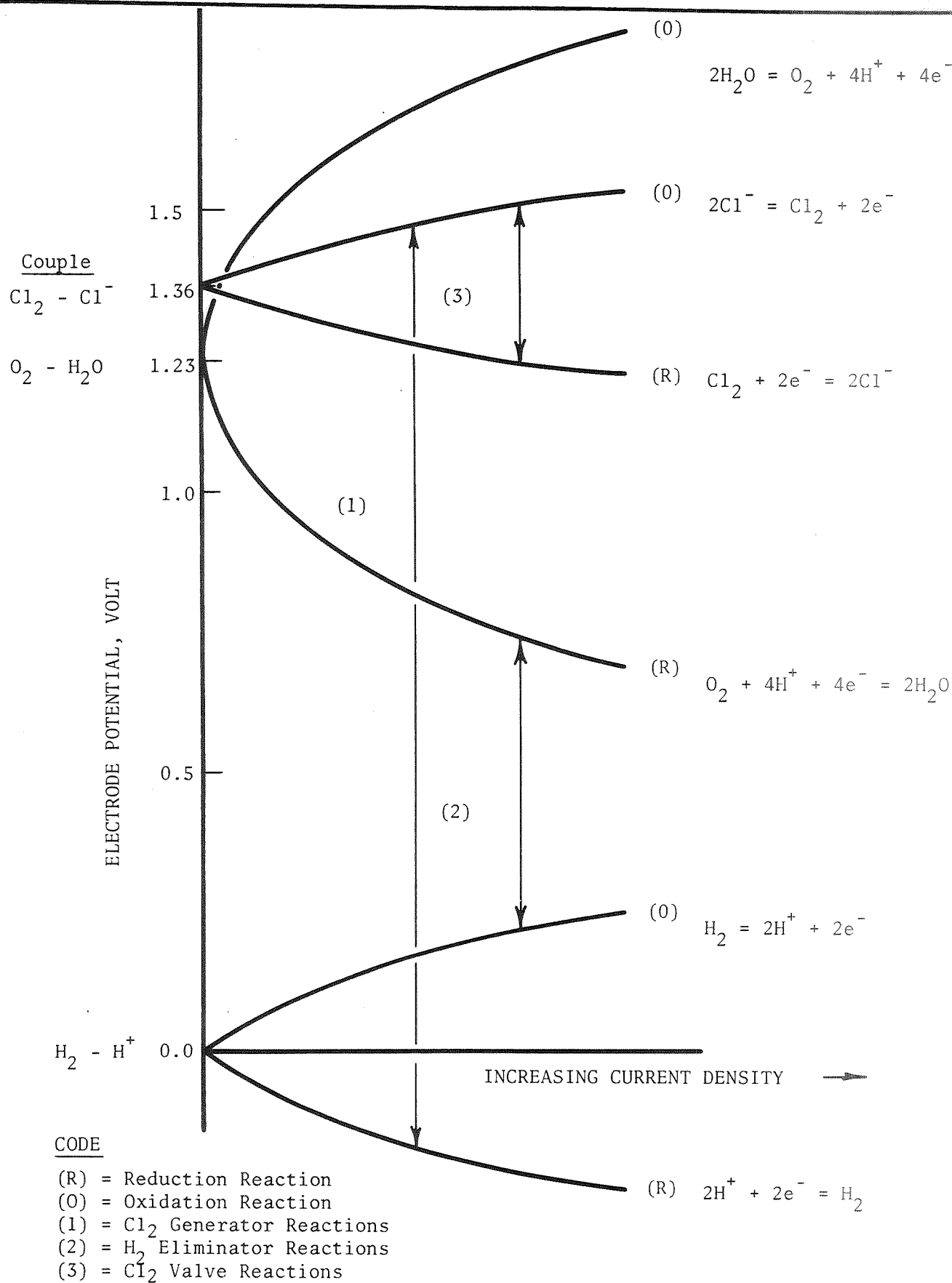


FIGURE A-1 COMPARISON OF REACTION RELATIONSHIPS

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